

INVESTIGATIONS ON CERTAIN METHODS OF ANALYSIS OF FATS AND RESINS.

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR
THE DEGREE OF

DOCTOR OF PHILOSOPHY

IN THE

UNIVERSITY FACULTY OF PURE SCIENCE

OF

COLUMBIA COLLEGE.

BY

PARKER CAIRNS MCILHINEY, PH. B., A. M.

CHEMICAL PUBLISHING CO.,
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INTRODUCTION.

The investigations recorded in this dissertation were undertaken with the idea of finding methods of analysis for varnishes. Before this work itself could be taken up it was necessary to ascertain how far the methods of analysis used for fats could be applied to resins and mixtures of oils with resins.

The methods depending upon the power of these substances to absorb halogens were first studied and in the course of the work a new method of analysis was developed by which not only is the power to absorb halogen by addition determined, but also the activity towards reagents is measured.

In the work on the processes involving saponification a process also believed to be new was used for determining the Koettstorfer figure of dark colored substances.

While working with rosin oil the action of nitric acid upon a number of oils was studied quantitatively with the result that a process was devised for effecting a fairly accurate separation between rosin oil and mineral oils for which no good method has hitherto been described.

In the actual analysis of varnishes a method was devised for the determination of volatile solvent and proved to be satisfactory, but in the analysis of the non-volatile portion the results were principally negative. They prove, however, that the methods of fat analysis are not applicable for this purpose.

For valuable suggestions and advice and for a number of samples which it would have been impossible to obtain elsewhere, thanks are due to Prof. A. H. Sabin.

PART I.

THE IODINE FIGURE OF ROSIN.

The first investigation was made upon the Hübl process as applied to resins. The resin about which our knowledge is most definite is common rosin. It is the residue obtained by distilling the oil of turpentine out of the turpentine obtained from several trees, principally the long-leaf pine, *Pinus palustris*, the loblolly, *Pinus taeda*, and the Cuban pine, *Pinus Cubensis*. (Rept. Sec. Agric., 1892, 334.) Chemically rosin consists of an acid or a mixture of acids of high molecular weight and related in some way to the terpenes.

Flückiger, *Jahresber. d. Chem.*, 1867, 727,

Emmerling, *Ber. d. chem. Ges.*, 12, 1441.

Haller, *Ber. d. chem. Ges.*, 18, 2165.

Liebermann, *Ber. d. chem. Ges.*, 17, 1884.

Ciamician, *Ber. d. chem. Ges.*, 11, 269.

Laurent, *Ann. Chem.*, 34, 272.

Duvernoy, *Ann. Chem.*, 148, 143.

Cailliot, *Jahresber. d. Chem.*, 1874, 629.

Vesterberg, *Ber. d. chem. Ges.*, 18, 1331.

Ber. d. chem. Ges., 19, 2167.

Ber. d. chem. Ges., 20, 3248.

In the analyses of oils, and especially drying oils, one of the most useful tests is the determination of the Hübl number. The iodine figure of rosin, which is a common adulterant of oils, is stated by Benedikt (*Analyse der Fette und Wachsarten*, 171) to be 115.7; Williams (*Chem. News*, 58, 224) gives 115.31 and 114.80 for refined rosin and 112.01 and 113.28 for ordinary. Mills (*Destructive Distillation*, 13) has determined the bromine absorption to be 112.7 per cent., which would correspond to an iodine absorption of about 179. In order to throw some light on the causes of this disagreement, experiments were made to ascertain the effect of different amounts of iodine in excess, different times of absorption, and different qualities of rosin.

Five samples were used representing different grades from "W.W." (water-white) rosin to "A" (black).

In the tests made to ascertain the influence of time and of excess of iodine the rosin used was that known as W. W., which is the best grade in the market. The iodine solution used contained twenty-five grams of iodine and thirty grams of mercuric chloride per liter, and the thiosulphate solution 24.8 grams of sodium thiosulphate per liter. The thiosulphate solution was standardized by means of a solution of potassium dichromate made from chemically pure dichromate which had been further purified by several recrystallizations. The tests were made in bottles of 250 cc. capacity, having carefully ground stoppers, such as are used in the assay of silver bullion. The rosin was in each case dissolved in ten cc. of chloroform and the absorption was effected in a dark closet.

The results were as follows:

Quality of rosin.	Quantity, grams.	Excess of iodine in cc. $\frac{N}{10}$ thio- sulphate.	Time of absorp- tion.	Iodine figure.
Water-white	0.3030	17.4	2 hours.	142.9
" "	0.3017	25.4	2 "	146.4
" "	0.3048	33.2	2 "	148.5
" "	0.3010	50.2	2 "	152.1
" "	0.3007	13.35	1 hour.	126.7
" "	0.3027	11.6	2 hours.	133.1
" "	0.3003	10.5	4 "	142.0
" "	0.3023	8.8	8 "	144.8
" "	0.3087	11.55	18 "	160.3
" "	0.3033	1.9	52 "	172.6
"A" (black).....	0.3055	20.25	18 "	143.6
"E"	0.3012	14.2	18 "	156.4
"G"	0.3054	13.7	18 "	153.1
"W. G." (window-glass)..	0.3160	9.7	18 "	164.2
"W. W." (water-white)...	0.3087	11.55	18 "	160.3

It appears from these results that the average iodine absorption in eighteen hours by different qualities of rosin is 155.5, the average quantity of rosin used being 0.3073 grams and the average excess of iodine equivalent to 13.88 cc. $\frac{N}{10}$ thiosulphate. The darker samples of rosin absorb less iodine than the lighter ones which have been subjected to less heat. The variations due to different lengths of time and different amounts of iodine in excess are, however, so serious that comparatively little can

be learned by Hübl's process as to the nature of an oil when rosin is present in any considerable quantity.

The next investigations were made upon a new process for determining the iodine figure, that of Gantter. It was thought that more reliable results might be obtained in this way as in his article he claims greater accuracy on account of the absence of mercuric chloride.

PART II.

GANTTER'S PROCESS OF DETERMINING THE IODINE FIGURE OF FATS.

F. Gantter (*Ztschr. anal. Chem.*, **32**, 178 and 181) proposes a new method of determining the iodine figure of fats and oils in which he uses carbon tetrachloride as a solvent for both the fat and iodine and uses no mercuric chloride as in the Hübl process. He states that the figures obtained when mercuric chloride is used depend upon the amount used. The results which he obtained and from whom he draws these conclusions are as follows:

Substance.	Amount iodine used.	Amount HgCl ₂ used.	Iodine figure.
0.100 gram linseed-oil....	0.100 gram.	0.050 gram.	83.5
" " " "	0.600 "	0.000 "	85.3
" " " "	0.150 "	0.250 "	141.0
" " " "	0.150 "	0.500 "	148.0
" " " "	0.600 "	0.250 "	156.4
" " " "	0.600 "	0.500 "	173.6
" " " "	0.600 "	1.000 "	188.4
" " lard	0.500 "	0.000 "	25.0
" " "	0.500 "	0.250 "	61.0
" " "	0.500 "	0.500 "	63.0
" " "	0.500 "	1.000 "	85.1

His results prove that the amount of mercuric chloride present influences the results and that a very large excess of Hübl's reagent would give a higher figure for linseed-oil than a moderate excess, but they certainly do not justify the conclusion which he draws from them that the use of mercuric chloride is unnecessary, and it is on this assumption that the accuracy of his process depends.

To ascertain whether fats would absorb from a solution of iodine alone in any suitable solvent as much iodine as would be necessary to convert them into saturated bodies, portions of a sample of oleic acid were treated with measured quantities of solutions of iodine in alcohol, carbon disulphide, and carbon tetrachloride. All these solvents dissolve both the oleic acid and iodine.

The results were as follows:

Solvent.	Amount of oleic acid.	Excess of iodine in cc. $\frac{N}{10}$ thio-sulphate.	Iodine figure.
Alcohol.....	0.9947 gram.	43.4	30.4
"	1.1445 grams.	43.5	26.1
Carbon disulphide ...	0.9791 gram.	58.9	52.7
" " ...	1.0044 grams.	59.0	51.3
Carbon tetrachloride.	0.1171 gram.	27.9	27.6
" "	0.1186 gram.	28.2	24.1

The iodine figure of the sample as determined by the Hübl process was 80.0.

These results show that iodine alone will not saturate fats and if it is used for this purpose its action must be assisted by mercuric chloride. Gantter's process, therefore, does not determine the iodine figure but an arbitrary figure which is not comparable with the results obtained by any other process.

PART III.

A NEW METHOD OF ANALYZING FATS AND RESINS.

A number of processes have been proposed and used for the analysis of fats depending upon the power possessed by their unsaturated constituents to absorb by direct addition two or four atoms of bromine or iodine.

Allen, *Analyst*, **6**, 177, proposed the use of an aqueous solution of sodium hypobromite to be added to a weighed quantity of the oil together with sufficient hydrochloric acid to liberate the bromine which then acts upon the oil. An excess having been added, its amount is determined with sodium thiosulphate after adding potassium iodide.

Mills and Snodgrass, *J. Soc. Chem. Ind.*, **2**, 436, added a solution of bromine in carbon disulphide to a solution of the fat in the same solvent until an excess has been added as indicated by the red color of the bromine remaining permanent for fifteen minutes, and then a solution of potassium iodide and determined the excess with thiosulphate.

Mills and Akitt, *J. Soc. Chem. Ind.*, **3**, 65, proposed to substitute carbon tetrachloride for carbon disulphide and to determine the excess by a solution of β naphthol in the same solvent.

Hübl, *Dingler's Poly. J.*, **253**, 281, and *J. Soc. Chem. Ind.*, **3**, 641, suggested the use of a solution containing twenty-five grams of iodine and thirty grams of mercuric chloride dissolved in one liter of alcohol, a known measure of the reagent to be added to a weighed portion of the oil and allowed to remain tightly stoppered for a certain length of time when the excess is determined with thiosulphate.

Levallois, *J. pharm. chim.*, 1887, **1**, 334, used bromine water, adding it, in just sufficient excess to slightly color the liquid, to the fatty acids obtained from the oil suspended in water.

Halphen, *J. pharm. chim.*, 1889, **20**, 247, used bromine water in excess determining the amount of excess with sodium hydroxide.

Gantter, *Ztschr. anal. Chem.*, 1873, 178, suggested the use, as a reagent, of iodine dissolved in carbon tetrachloride.

The aim of all these processes is to determine the amount of halogen which the substance under examination will absorb by addition, but the figures obtained represent this only approximately even when substances which easily form substitution products are absent. Some substitution takes place with almost all oils, and with rosin oil, rosin, and probably most other resins, substitution causes the entire absorption.

The extent to which this substitution takes place depends upon the nature of the substance operated upon, and varies with different oils and resins, and a determination of the amount of halogen so absorbed may serve as a means of identifying and in some cases determining them.

The following process has been devised for determining the

amount of bromine which oils and resins can absorb by addition, (which will be called the "Bromine-Addition Figure"), and at the same time the amount of bromine which replaces hydrogen, the action being allowed to continue eighteen hours in the dark; this gives the "Bromine-Substitution Figure." The first figure gives in most cases the same information as the Hübl figure but is more reliable, while the second figure is a measure of the activity of the saturated constituents toward bromine.

It depends upon the fact that bromine in forming substitution compounds forms a molecule of hydrobromic acid for every atom of bromine which replaces hydrogen, while in forming additive compounds no hydrobromic acid is formed.

It was found impossible to use iodine alone as the addition figures are then very much too low and there is little difference between the substitution figures of bodies of unlike character.

The following solutions are used:

Bromine in carbon tetrachloride.....	$\frac{N}{3}$
Sodium thiosulphate.....	$\frac{N}{10}$
Potassium hydroxide.....	$\frac{N}{10}$

0.250-1.000 gram of the substance is dissolved in ten cc. of carbon tetrachloride in a bottle of 500 cc. capacity provided with a carefully ground glass stopper. An excess of bromine solution is added, the bottle tightly stoppered and placed in a dark closet. No water or alcohol should be present and light should be excluded as far as practicable. At the end of eighteen hours the bottle is cooled with ice to form a partial vacuum, and a piece of wide rubber tubing about one and one-half inches long is slipped over the lip of the bottle so as to form a well about the stopper. This well is filled with water and the stopper carefully lifted when the water will be sucked into the bottle and dissolve the hydrobromic acid present. When about twenty-five cc. of water have been added in this way, the bottle is well shaken and 10-20 cc. of twenty per cent. potassium iodide solution added. The excess of bromine acts on the potassium iodide, liberating a corresponding amount of iodine which is titrated with $\frac{N}{10}$ thio-sulphate after adding about seventy-five cc. more water, using starch as an indicator. The total bromine absorption is calcu-

lated from the difference between the amount of thiosulphate required for the bromine solution added and the amount required for the excess. The contents of the bottle are now transferred to a separatory funnel and the aqueous portion separated. filtered through a cloth filter, a few drops of thiosulphate added if the solution is blue, and this is then titrated with $\frac{N}{10}$ potassium hydroxide using methyl orange as indicator. The end reaction is best observed by using a porcelain casserole to contain the solution, adding the alkali in slight excess and titrating back with $\frac{N}{10}$ hydrochloric acid until the pink acid tint just reappears. From the number of cubic centimeters of alkali used the amount of bromine present as hydrobromic acid is calculated, and when expressed in per cent. gives the bromine-substitution figure because for every atom of bromine which has replaced an atom of hydrogen, one molecule of hydrobromic acid has been formed. Twice the bromine-substitution figure subtracted from the total absorption gives the bromine-addition figure.

The following results were obtained:

Substance.	Total bromine absorption, eighteen hours.	Bromine- addition figure.	Bromine- substitution figure.
W. G. Rosin.....	212.7	0.0	106.35
E. Rosin.....	206.5	0.0	103.25
Second run Rosin Oil (a).....	116.2	0.0	58.1
“ “ “ “ (b).....	114.7	0.0	57.35
American Raw Linseed-Oil ...	102.88	102.88	0.0
Same Oil Boiled.....	103.92	103.92	0.0
White Salad Cotton-seed Oil..	65.54	64.26	0.64
Sperm Oil	56.60	54.52	1.04

A consideration of the above figures shows that the results are much more instructive than those obtained by the Hübl process which is the one in common use. Rosin oil, rosin, and other resins may be detected and determined in mixture with fatty oils, or, if they are present in known quantity, the character of the fatty oil may be determined. Investigations which are being made on a large number of oils and resins will probably furnish analytical data for the analysis of oils and varnishes.

PART IV.

THE QUANTITATIVE SEPARATION OF ROSIN OIL FROM MINERAL OILS.

These two oils being both unsaponifiable are usually determined together as "unsaponifiable material" in the analysis of oils. They may be distinguished from one another by several methods.

1. *The Specific Gravity*.—Rosin oil has a much higher gravity than mineral oils varying from 0.960 to 1.000 while heavy mineral oils range from 0.850 to 0.920.

2. *Valenta's Test*.—*Dingler's Poly. J.*, **252**, 297, and **253**, 418, *J. Chem. Soc.*, **48**, 93. Glacial acetic acid dissolves 2.67–6.50 per cent. by weight of mineral oil while rosin oil is soluble to the extent of 16.87 per cent. Mixtures, however, do not dissolve in proportion to the amount of rosin oil present.

3. *The Stannic Bromide Test*.—Allen, *Comm. Org. Anal.*, **2**, 463. A solution of stannic bromide in carbon disulphide gives, with small quantities of rosin oil in carbon disulphide solution, a purple coloration, while mineral oils do not.

4. *Solubility in Acetone*.—Demski and Morawski, *Dingler's Poly. J.*, **258**, 39. Acetone is miscible with rosin oil in all proportions while mineral oils require several volumes for solution.

5. *The Elaidin Test*.—Hager, *Ztschr. anal. Chem.*, **19**, 116. Rosin oil gives a dark red clear liquid while mineral oils remain unchanged.

6. *Ammonia Emulsion Test*.—Hager, *Muspratt's Tech. Chemie.*, 1893, **4**, 127, mixes two cc. of the oil to be tested with two cc. of petroleum benzene and four cc. of water and after shaking adds one cc. of ten per cent. ammonia; he then shakes violently and allows to stand for one to two hours. A persistent milky layer indicates rosin oil.

7. *Action of Sulphuric Acid*.—Hager, *Ztschr. anal. Chem.*, agitates a portion of the oil with an equal volume of concentrated sulphuric acid for five minutes and then pours into several volumes of cold water. Mineral oil gives a white milky liquid

which separates into two clear light-colored layers. Rosin oil gives a gray or brownish milky liquid which separates an upper layer of yellow brown color full of opaque flocks.

8. *The Color Produced with Sulphuric and Acetic Acids.*—Storch, *Analyst*, **13**, 71. Two cc. of the oil is shaken up with one cc. of anhydrous acetic acid and warmed gently. After cooling, the acetic liquid is removed with a pipette and a drop of strong sulphuric acid added which immediately produces a brilliant red color if any rosin oil is present. Cholesterin in many fatty oils gives a similar reaction. The same author determines rosin oil quantitatively by its solubility in alcohol which is greater than that of mineral oils.

9. *The Hübl Figure.*—Valenta, *Dingler's Poly. J.*, **253**, 420. The Hübl figure of rosin oil is forty-three to forty-eight, while that of mineral oils is below fifteen.

10. *The Refractive Index.*—Holde, *Mittheil d. chem. tech. Vers. Anst.*, 1890, **8**, 269. With the Abbe refractometer the indices are as follows:

Rosin oil.....	1.5344
Mineral oils.....	1.4923

11. *Mauwene's Test.*—*Muspratt Tech. Chem.*, 1893, **4**, 128. Rosin oil gives a rise of temperature of 42° C. Mineral oils only a slight rise. Allen, *Comm. Org. Anal.*, **2**, 462, says the rise in temperature of rosin oil is 18–20° C.

12. *The Action of Nitric Acid.*—*Muspratt*, **4**, 127. Nitric acid of 1.185 sp. gr. when heated with rosin oil reacts violently with it giving off copious red fumes while mineral oils are but slightly effected.

Allen, *Comm. Org. Anal.*, **2**, 462, says that cold nitric acid is sometimes without immediate action on rosin oil but on warming a violent reaction often very suddenly ensues and after cooling the rosin oil is found to have been converted into a more or less brittle red resin.

This process was investigated with a view to making it quantitative. Attempts were made to use nitric acid of 1.42 sp. gr. at a boiling temperature, but the frothing of the mass proved a serious difficulty, the liquid in every instance frothing out of the

flask. Acid of 1.2 sp. gr. was found more manageable, the frothing in this case being slight. It was thought that the red resin might be dissolved in alkali, in which it appears to be quite soluble, and leave behind the mineral oil which could be dissolved in benzene, but this process could not be made to work satisfactorily. It was found, however, that the red resin produced from the rosin oil was insoluble in petroleum ether while mineral oil dissolves easily.

The process was therefore altered by diluting the products of the reaction with water and extracting with petroleum ether.

The following process gave satisfactory results:

Fifty cc. of nitric acid of 1.2 sp. gr. are heated to boiling in a flask of 700 cc. capacity. The source of heat is removed and five grams of the oil to be analyzed added. The flask is then heated on the water-bath, with frequent shaking, for fifteen to twenty minutes, and about 400 cc. of cold water added. After the liquid has become entirely cold, fifty cc. of petroleum ether are added and the flask agitated. The oil which remains unacted upon dissolves in the ether, while the resin remains in suspension. The liquid is poured into a tapped separator, leaving the lumps of solid resin as far as possible behind in the flask. After settling, the aqueous liquid is drawn off and the ethereal layer poured into a tared flask. Another portion of petroleum ether is added to the resin remaining in the flask and allowed to act upon it for about ten minutes, when it is added to that in the tared flask. After distilling off the ether the oil is weighed. Mineral oils lose about ten per cent. in this way, and hence the weight of oil found must be divided by 0.9 in order to find the amount present in the sample analyzed.

Allen found mineral oils to lose ten to twelve per cent. on treatment with nitric acid. *Pharm. Jour.*, 3 series, **11**, 266.

A mixture of seventy-six per cent. of mineral oil with twenty-four per cent. of rosin oil gave, by this method, 76.8 per cent. of mineral oil.

PART V.

A METHOD OF DETERMINING THE KOETTSTORFER FIGURE OF DARK COLORED SUBSTANCES.

The Koettstorfer figure of a fat or resin is the number of milligrams of potassium hydroxide required to saponify one gram of the substance. It is determined by adding to a weighed quantity of the substance a measured excess of an alcoholic solution of potash, evaporating off the alcohol, redissolving in neutral alcohol, and determining the excess of potash by standard hydrochloric acid. When the substance is light in color and the alcohol free from aldehyde, the determination is easily made, but if the substance has much color of its own the end reaction with phenolphthalein is indistinct. The same is true if the alcohol used contains aldehyde, as this gives with caustic potash a red brown color. The latter difficulty can be surmounted by purifying the alcohol, but the former one is more serious. In experimenting to find a mode of procedure which would obviate the difficulty it was observed that a solution of neutral soap, to which ammonium chloride had been added, when submitted to distillation liberated a quantity of ammonia equivalent to the alkali combined with the soap.

Based on this principle the following method was devised: Two grams of the substance under examination is weighed into an Erlenmeyer flask, an excess of an alcoholic solution of caustic soda added, and the alcohol evaporated off. 250 cc. of ninety-three per cent. alcohol is now added and the solution heated until the soap is dissolved. Carbonic acid gas is now passed through the solution for about one hour. This treatment converts the free caustic alkali present into carbonate and bicarbonate which precipitate. The solution is then filtered into a suitable flask and most of the alcohol distilled off. It is necessary to add a spiral of platinum wire or a piece of sharp pointed metal or glass to prevent boiling over. When most of the alcohol is gone a solution of ten grams of ammonium chloride, in 100 cc. of

water, is added and the solution distilled as far as possible, the distillate being caught in twenty cc. of normal hydrochloric acid which is titrated at the end of the operation, using methyl orange as indicator. The amount of hydrochloric acid neutralized by ammonia is equivalent to the combined alkali in the test.

Alcohol of ninety-three per cent. was found to dissolve sodium bicarbonate sufficient to neutralize 0.34 cc. of normal acid for every 100 cc. of alcohol used. A deduction must therefore be made for this in the calculation.

A sample of linseed-oil tested in this way gave a Koettstorfer figure of 192.4, and by the ordinary process the figure found was 193.1. A sample of dragon's blood resin gave 124.9.

PART VI.

THE ANALYSIS OF VARNISHES.

At present varnishes are seldom analyzed because no means are known of determining with any approach to accuracy the amounts of the substances composing them. The tests used are practical ones and usually consist in varnishing a suitable surface with the sample to be tested and subjecting the varnished object to treatment as nearly as possible like that which it will receive in practice. If it is desired to ascertain the proportions of the different constituents, practical varnish-makers claim to be able to make up samples which will match in properties one to be tested, and in this way to arrive at the proper result. However this may be, it is out of the question for the chemist who is not a varnish-maker to use such a process. If methods can be devised whereby a chemist can make an actual analysis with a fair degree of accuracy, buyers can be certain of what they purchase and manufacturers can work more intelligently.

The different kinds of varnish may be classified as follows:

1. Spirit varnishes.
2. Volatile oil varnishes.
3. Fixed oil varnishes.
4. Miscellaneous; collodion varnishes, etc.

Spirit varnishes are composed of a resin dissolved in alcohol. Shellac spirits, made by dissolving shellac in wood or grain alcohol, is the most common.

Volatile oil varnishes are made by dissolving a resin in turpentine. Dammar varnish is a good example. Benzine is largely used as a substitute for turpentine in this and other varnishes.

The most important class is the fixed oil varnishes, and it is the analysis of this sort which will be considered. They are made from linseed-oil, a resin, and turpentine.

The principal resins used are kauri, manilla, and hard copals, such as Zanzibar. Common rosin is largely used as an adulterant. Kauri is the resin used by far the most, and there are many grades, varying in price from three cents to sixty cents a pound. Manilla stands next in the amount used, and of the others comparatively small quantities are used.

The resins used in fixed oil varnishes are in their natural state insoluble in linseed-oil and in turpentine. It is only after undergoing a process of roasting or distillation that they become soluble, and in this operation they lose from twenty to twenty-five per cent. in weight. In the process of manufacture the resin is first melted down in a kettle, and after it has been sufficiently heated the proper quantity of linseed-oil, also hot, is added, and the mixture heated some time longer to effect a combination between the oil and resin. After cooling somewhat, sufficient turpentine is added to properly thin the varnish.

It is difficult for several reasons to obtain samples of varnish for experiment in which the proportion of the constituents is known. They cannot be made successfully in small quantities as they are then of poor quality, and results obtained from such samples cannot be trusted. Through the kindness of Prof. A. H. Sabin, three samples of varnishes of known composition were obtained for experiment.

The Determination of Turpentine.—H. J. Phillips (*Chem. News*, **63**, 275, and *J. Soc. Chem. Ind.*, **10**, 577) proposes to distill off the turpentine at 220° C., using about 150 grams of varnish and catching the distillate in a tared flask. A current of coal-gas is passed through the liquid to prevent oxidation of the linseed-oil, and at the same time to assist in the removal of the turpentine vapor by carrying it away as fast as formed, and by agitating the liquid. The method is open to several objections;

any vapors of naphtha in the coal-gas used are likely to be caught and contaminate the turpentine. This difficulty would be overcome by the use of carbon dioxide instead of coal-gas, but carbon dioxide is not usually available in sufficient quantity. The author does not use any condenser, but depends upon the cooling of the neck of the retort used, by the air, which is not sufficient. The residue left after most of the turpentine is gone is very viscous and retains some turpentine very persistently.

Mills (*J. Soc. Chem. Ind.*, **5**, 222) says that the volatile constituents of varnish are easily determinable by evaporation with water.

Attempts were made to effect the removal of turpentine by distilling it off in a vacuum. Trials were first made using twenty-five grams of substance and a temperature of 100° – 120° C., but this proved to be much too low a temperature and it was subsequently found that by using five grams instead of twenty-five grams of substance the results were better.

The method used was as follows: A portion of the varnish is weighed into a tared, round-bottom flask which is then heated in a paraffin bath at a temperature of 180° C. for four to eight hours, the air and vapor being removed from the interior of the flask by a pump. The flask is then again weighed and the loss in weight represents turpentine.

The results by this method were as follows:

Varnish used.	Per cent. of turpentine found.	Per cent. present.	Quantity of substance used.
A.....	52.7	60.0	25 grams.
B.....	34.9	41.4	25 "
C.....	52.7	56.9	5 "

The results are thus seen to be too low and irregular, and the residues smelled of turpentine. It was found that these traces of turpentine could be removed, and correct results obtained by adding to the contents of the flask after cooling two or three cc. of petroleum ether of very low boiling-point, allowing the residue to dissolve, and then carefully exhausting the flask of air, and finally heating gently. Of course, in these experiments it is necessary to use round-bottom flasks. The great objections to this method are that it does not distinguish between turpentine

and any other volatile substance, and also that it requires arrangements for exhausting air, which are not always available. The non-volatile residue is, however, in the very best condition for further examination.

Another method which has been used is a determination of the loss in weight on evaporating off the turpentine in the air-bath at 100° C. from a quantity of varnish contained in a watch-glass. This method is open to the same objections as the previous process, and the residue is not in good condition for further examination on account of the drying of linseed-oil. The fact that linseed-oil increases in weight on exposure to the air tends to give too low results. The formation of a film of dried varnish preventing further evaporation renders it necessary to use only small quantities of substance. In experimenting with the process it was found better to use watch-glasses of flat form than the ordinary concave ones. Three-quarters to one hour exposure at 100° and 0.400 to 0.500 gram substance gave the best results.

The following figures were obtained in this way:

Varnish.	Amount found.	Amount present.
B.....	40.8	41.4
C.....	56.0	56.9
D	53.4	56.8

The requirements of a satisfactory process for determining turpentine are:

(1) That the volatile material shall be separated under conditions which admit of its being actually weighed or measured and then submitted to further treatment.

(2) That the non-volatile portion shall be subjected to as little heat as possible, both to avoid any destructive distillation and to leave it unaltered for further examination.

(3) The process should require no unusual apparatus. None of these processes fulfill the above conditions.

It is well known that on distilling together two immiscible liquids, such as carbon disulphide and water, the boiling-point of the mixture is lower than that of the more volatile liquid. Carbon disulphide boils at 49° , but when distilled with water the boiling-point of the mixture is 43° (Kundt, *Jahresb. Fort. Chem.*, 1870, 49).

On distilling together 100 cc. of water and five cc. of turpentine it was found that the first ninety-five cc. of distillate contained all the turpentine which separated very well from the water. Experiment showed that ninety cc. of water either dissolve or hold in suspension permanently about 0.3000 gram of turpentine. On these principles the following process was devised:

Twenty-five grams of varnish are weighed into a flask of 400 cc. capacity, in which has been placed a piece of granulated tin, or its equivalent, to prevent bumping and about ten cc. of water. The flask is in this way prevented from becoming greasy, which would cause violent bumping.* The contents of the flask are now submitted to distillation, the distillate being caught in a tapped separator. When ninety or ninety-five cc. of water have come over, the distillation is stopped and the turpentine and water allowed to separate. If the contents of the flask still retain any odor of turpentine more water should be added and the distillation resumed. After settling for a sufficient length of time the water is carefully drawn off and the turpentine poured into a tared flask and weighed. A correction is made for the amount of turpentine retained by the water, amounting to 0.300 gram for ninety cc. of water. In some experiments salt was added to the water to raise its boiling-point, but no apparent advantage was gained except when the non-volatile residue was heavier than water; in this case the salt prevented the residue from sinking to the bottom and causing bumping by greasing the flask. If it is desired to examine the residue the remaining water is poured off from it and alcohol added. On distilling off the alcohol, and if necessary removing the last of it by the addition of a little ether, which is also evaporated off, the residue is obtained pure.

The following results were obtained by this process:

Varnish.	Per cent. found.	Per cent. present.
B.....	41.2	41.4
C.....	57.1	56.9
D	56.3	56.8

The sample D was made by dissolving common rosin in turpentine, and it was therefore more difficult to remove the last

* 90 c c. of water is now added.

trace of turpentine from the non-volatile residue than it ever is in an oil varnish, but even in this case the result is fairly accurate.

The method requires no unusual apparatus and can be carried out in about half an hour. The residue is not heated above the boiling-point of water, and the turpentine is actually weighed and may be itself analyzed.

For the determination of benzene in turpentine, the method of Burton (*Am. Chem. J.*, **12**, 102) gives the best results. It depends upon the conversion of turpentine into acids soluble in water by the action of nitric acid while benzene remains unaffected and is separated and measured or weighed.

The Non-volatile Portion.—The analysis of the residue consisting of linseed-oil and resin, both more or less altered by heat, presents an extremely difficult problem in proximate analysis and one which yet remains unsolved.

The properties of resins have been investigated analytically by ;

Hirschsohn, *Pharm. Ztschr. f. Russland*, 1875, 225, and 1877, 1; *Pharm. Jour.*, **7**, 369, and **8**, 389.

Schmidt and Erban, *Sitz. d. Wiener. Akad.*, **94**, 917, and *Ztschr. angew. Chem.*, 1889, 35.

Mills, *J. Soc. Chem. Ind.*, **5**, 222.

Mills and Muter, *J. Soc. Chem. Ind.*, **4**, 96.

Williams, *Chem. News*, **58**, 224.

These investigators have made upon various resins the same tests which have been used in the analysis of oils; *viz.*, the acid figure, the Koettstorfer figure, the iodine figure, the per cent. of bromine absorbed, and the solubility in ether, alcohol, etc. Their results are given in the following table :

Resin.	Variety.	Acid figure.	Koettstorfer figure.	Hübl Per cent. bromine absorbed.	Observer.
Amber ...		15.4	86.8	62.1	Williams.
" ...			160.7		Mills.
" ...			145.0		Schmidt and Erban.
" ...			144.6		" " "
" ... Melted		0.0	38.9	4.8	" " "
" ... "		0.0	33.9		" " "
Animi ... Rough Demarara		26.6	73.6	127.88	Williams.
" ... Fine Zanzibar		18.2	73.6	135.25	"
" ... Unknown		25.2	87.5	137.54	
" ...			95.4		60.22 Mills.

Resin.	Variety.	Acid figure.	Koetts- torfer figure.	Hübl figure.	Per cent. bromine absorbed.	Observer.
Copal	Soft manilla	131.6	184.1	137.79		Williams.
"	Borneo manilla	141.4	176.7	138.04		"
"	Singapore manilla	128.8	194.1	123.31		"
"	Cleaned Sierra Leone ..	84.0	129.0	138.04		"
"	Rough Sierra Leone....	72.8	138.5	133.35		"
"	Rough Accra	46.2	131.6	121.66		"
"	Rough White Cengola..	57.4	133.0	129.66		"
"	Fine Clean Red Cengola	60.2	136.2	136.90		"
"	Unknown	57.4	122.2	142.24		"
"			123.9		83.93	Mills.
"	Reduced to $\frac{3}{4}$ by boiling, ..		128.9		84.52	"
"	Boiled	114.4				"
"	Zanzibar		92.4			Schmidt and Erban.
"	"		89.6			" " "
"	" melted	0.0	36.8			" " "
"	"	0.0	34.6			" " "
"	White Angola		132.2			" " "
"	"		129.7			" " "
"	" melted ..	93.6	118.8	44.9		" " "
"	" ..	93.4	117.8			" " "
"	Red Angola.....		148.0			"
"	"		146.4			"
"	" melted	30.5	110.7	34.8		"
"	"	30.0	109.8			"
Dammar, Batavia		22.4	36.4	117.67		Williams.
"	Unknown	26.6	31.1	142.24		"
"			52.3		117.94	Mills.
"		33.0	47.1	63.6		Schmidt and Erban.
"		30.6	46.5	63.5		" " "
Elemi		15.7	28.6	175.39		Williams.
"			32.9		122.23	Mills.
"		22.3	25.1	85.1		Schmidt and Erban.
"		22.0	24.0	80.9		" " "
Kauri	Medium.....	63.0	99.3	151.13		Williams.
"	Fine	51.8	77.4	164.21		"
"			128.8		108.22	Mills.
Rosin....	Refined	179.2	187.4	115.31		Williams.
"	"	177.8	195.7	114.80		"
"	Ordinary.....	169.4	176.4	112.02		"
"	"	166.6	190.1	132.28		"
"	Refined		181.0		112.7	Mills.
"	Average of 5 samples ..			155.5		McIlhiney.
"	Window glass	159.1	170.4			"
"	E.	168.5	189.9			"
"	A. Black.....	155.7	195.1			"
"		146.5	168.2	116.8		Schmidt and Erban.
"		145.5	166.0	114.6		" " "

The corresponding figures for linseed-oil are as follows :

Acidity should be o.o. Mills allows one per cent. KOH for acidity.

Koettstorfer figure (Allen, *Commercial Organic Analysis*, 2, 42). Nine samples, 187.4-195.2.

Hübl figure (Allen, *loc. cit.*, 50). Raw oil, 155-160; boiled oil, 148. Holde, *Mittheil. K. tech. Vers. Berlin*, 1891, 9, 81, and *J. Soc. Chem. Ind.*, 12, 179-180, 954.

Bromine absorption (Levallois, *J. pharm. chim.*, 1887, 1, 334), 100 per cent.

Mills (*J. Soc. Chem. Ind.*, 2, 436). Raw oil, 76.09 per cent.; boiled oil, 102.36 per cent.

McArthur (*J. Soc. Chem. Ind.*, 7, 64). Raw oil, 65.0-65.3 per cent.; boiled oil, 63.2-66.3 per cent.

The differences in solubility between linseed-oil and melted resins are but slight and are of little value in effecting separations in varnish analysis.

The Hübl figure is evidently useless as a means of quantitative analysis for the figures of linseed-oil and kauri the most frequently occurring resin, are almost identical.

The difference between the Koettstorfer figure is only about seventy-five, and even supposing that the figures of both oil and resin are known accurately, which is not the case, it would be difficult to make the analysis so carefully that the percentages of oil and resin would be correct.

Mills states that the analysis may be made by determining the acidity to phenolphthalein, and this proved to be correct, provided the mixture is composed of common rosin and linseed-oil and is not heated long. An analysis of such a mixture gave correct results but on attempting to apply the process to properly made varnishes the process was unsuccessful. Ten grams of a sample of varnish, known to contain 14.36 per cent. of kauri-resin, were diluted with a mixture of absolute alcohol, ether, and petroleum ether to obtain a clear solution and then titrated with a solution of caustic soda in alcohol using phenolphthalein as indicator. The acidity found in this way was equal to only 0.345 per cent. of potassium hydroxide; this would mean an acidity of 2.40 per cent. for the kauri present, whereas Mills found 11.44 per cent., and Williams 6.3 per cent. Mills' statement that "it is evident that boiled oil when heated with a resin makes no

difference in the resin's acidity," is not sustained by the facts.

The amount of bromine absorbed, as determined by the methods of Allen, Mills, and Levallois, is of no more use than the Hübl figure. The results depend largely upon the conditions under which the analysis is conducted.

In view of the fact that the bromine-addition figure of rosin is 0.0, while that of linseed-oil is 102, it seemed very likely that by means of this figure it would be possible to analyze varnish residues. To test the process, a mixture was made of fifty per cent. common rosin and fifty per cent. oleic acid. The bromine-addition figure of the oleic acid used was 51.78 per cent., and that of the mixture 25.7 per cent., corresponding to 49.6 per cent. of oleic acid instead of fifty per cent. In order, if possible, to obtain samples of boiled oil and kauri-resin in the same condition in which they are present in varnishes, a quantity of boiled oil was heated in a retort to a temperature of 290° C. and maintained at this temperature for one hour. A sample of clear kauri-resin was also heated in a retort until it had lost twenty-three per cent. of its weight. The non-volatile part of a varnish of known composition was analyzed at the same time. The figures obtained were as follows:

Substance.	Bromine-addition figure.	Bromine-substitution figure.
Heated linseed-oil	76.62	4.82
Melted kauri-resin	21.53	80.31
Non-volatile of varnish C.....	89.16	22.84
Kauri, 54.3 per cent., oil, 45.7 per cent..		
Theoretical figures of above.....	46.71	45.81

The process therefore fails to give any means of making this analysis on account of changes made by the process of manufacture in the properties of oil and resin. It is well-known to varnish-makers that heating together, effects remarkable changes in their physical properties, and that a certain amount of heating is necessary to make them knit together and work properly in the finished varnish.

Gladding (*Am. Chem. J.*, **3**, 416), has devised a process for determining common rosin in mixtures with fatty oils, depending upon the solubility of silver resinate in ether and the insol-

bility of silver oleate in the same medium. This process was tried on varnish but also failed to give satisfactory results. A varnish known to contain 14.36 per cent. of Kauri resin gave 25.9 per cent.

It is evident that the processes used in oil analysis are not adapted to the analysis of varnishes. The oil and resin react upon each other in some way not understood, giving rise to new compounds, and we must know something about what these compounds are before the analytical problem can be solved.

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